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Studies in the setting of polyelectrolyte materials

Part IV *The effect of sodium chloride and artificial saliva on the setting and compressive strength of glass-polyalkenoate and zinc polycarboxylate dental cements*

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The setting behaviour and compressive strengths of zinc polycarboxylate and glass polyalkenoate dental cements activated with sodium chloride solutions of different concentrations and also with artificial saliva have been studied. The results show that the effect of sodium chloride in these cements is concentration dependent. Saturated brine so increased the speed of set of the zinc polycarboxylate that the cement became impossible to mix. Conversely, while having little effect on the speed of setting of the glass polyalkenoate, saturated brine caused the compressive strength to fall to 18 MPa (from 85 MPa with pure water). Neither of the low-concentration solutions (i.e. 0.154 M NaCl or artificial saliva) showed any significant effects on the strength of either cement but both were found to speed up the rate of the setting reaction slightly and to sharpen the set. This effect was too slight to be a source of serious practical concern when these materials are used in clinical dentistry.

1. Introduction

The two polyelectrolyte cements widely used in dentistry are the zinc polycarboxylate and the glass polyalkenoate ("glass-ionomer") [1]. As part of continuing studies on the setting chemistry of these cements, one of the authors has recently shown that the presence of sodium salts alters the rate of the setting reaction of these cements and also affects their compressive strengths when set. Moreover, the effects in zinc polycarboxylate were found to be radically different from those in glass polyalkenoates [2].

Sodium salts in general, and NaCl in particular, have two related effects on the setting reaction. First, they alter the conformation adopted by the poly(acrylic acid) molecules in solution, due to electrostatic shielding of the functional groups [3]. Secondly, they affect the quality of water as a solvent, albeit by a mechanism that is not well understood [4], and this in turn affects the conformation of the polymer, as well as the ability of the water to solvate reacting species. In the case of the zinc polycarboxylate, these effects generally resulted in a faster reaction, but essentially the same final structure, hence the same strength. By contrast, for glass polyalkenoates, it led to a very slight reduction in the speed of the setting reaction, but to large differences in the final strength.

The aim of the present work was to extend this initial study by considering in more detail the effect of sodium chloride. First, the study aimed to establish the effect of varying the concentration of sodium chloride in the water used to activate the setting. Having previously used pure water (i.e. zero concentration) and a 1 M solution, the present study concerned both a very dilute solution, namely 0.154 M, i.e. physiological saline, and the most concentrated possible solution, saturated brine. This latter solution is approximately 6.1 M in NaCl [5]. Secondly, the study aimed to establish whether this recently discovered effect of electrolytes on the setting and strength of cements has any practical consequences. In other words, does contamination of a polyelectrolyte cement with saliva, a solution of *inter alia* sodium salts, affect the setting process and/or final strength of the restoration? Conventional advice to clinicians is to avoid contamination of cements with saliva, since this is known to wash out the reacting ions [6]. Whether this is the only effect, was tested by experiments carried out using what might be considered the worst possible case, i.e. using artificial saliva as the activating solution.

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2. Materials and methods

The cements used, as previously [2], were Aquakent, a glass polyalkenoate luting cement, and polykent, a zinc polycarboxylate (both ex. Kent Dental Ltd, UK), both of which are formulated from poly(acrylic acid). Each was mixed by hand at the powder:liquid ratio recommended by the manufacturer (Aquakent, 3.6:1 by mass; Polykent, 7.5:1).

For the aqueous phase, a range of concentrations of sodium chloride solutions, as well as demineralized water, were used to activate the setting of the cements. The details of the solutions employed are given in Table I, and the composition of the artificial saliva is given in Table II.

Working and setting times at 21 °C were determined in duplicate using the oscillating rheometer, described in detail elsewhere [1]. The working time was taken as the point at which the oscillation reached 95% of its initial amplitude; the setting time, the point at which it reached 5%.

Compressive strengths were determined as described in the appropriate British Standard [7]. In this method the compressive strength was determined at 24 h using a set of six samples of size 12 mm high × 6 mm diameter, stored initially in the mould at 37 °C for 1 h, then removed and stored in water, again at 37 °C, for a further 23 h. Specimens were tested on a Universal Testing machine (Instron 1180), using a crosshead speed of 1 mm/min. Compressive strength was determined from load at failure under these conditions.

Statistical analysis of the strength data was carried out using Student's *t*-test.

TABLE I Liquids used to activate cements

Activating liquid
Pure water
1 M NaCl
0.154 M NaCl
Saturated NaCl
Artificial saliva

TABLE II Composition of artificial saliva [8]

Component	Concentration (g/1)
Nacl	0.50
$NaHCO_3$	4.20
$NaNO_2$	0.03
KCl	0.20

3. Results and discussion

The working and setting times for the glass polyalkenoate and the zinc polycarboxylate are given in Table III and IV, respectively. Data previously reported for pure water and 1 M NaCl are also included [2].

In the case of the glass polyalkenoate, both 0.154 M NaCl and artificial saliva reduced the working time, but in each case, to only a slight extent. In terms of the sharpness of the set, the 0.154 M NaCl made very little difference, whereas the artificial saliva reduced the sharpness. The saturated brine made a considerable difference to both working and setting times, extending the working time by 1.3 min and the setting time by 8.4 min. The sharpness of the set was also considerably reduced. By contrast, as noted previously [2], the various NaCl solutions speed up the setting of zinc polycarboxylate, so much so that with saturated brine, the cement set too quickly to be mixed. Even the very low concentration of 0.154 M NaCl made a considerable difference to the speed of the setting reaction, reducing the working time by 1.1 min and the setting time by 6.6 min. Artificial saliva had slightly less effect, though in the same direction, and both solvent systems gave sharper sets than did pure water.

TABLE III Working and setting times of glass polyalkenoate

Activating liquid	Working time (min)	Setting time (min)	ST:WT
Pure water	3.3	14.5	4.4
0.154 M NaCl	3.0	13.4	4.5
1 M NaCl	3.3	16.2	4.9
Saturated NaCl	4.6	22.9	5.0
Artificial saliva	2.8	13.9	5.0

TABLE IV Working and setting times of zinc polycarboxylate

Activating liquid	Working time (min)	Setting time (min)	ST:WT
Pure water	3.5	13.9	4.0
0.154 M NaCl	2.4	7.3	3.0
1 M NaCl	3.0	7.9	2.7
Saturated NaCl	not mixable	–	–
Artificial saliva	3.1	9.4	3.0

The compressive strengths for the series of glass polyalkenoate cements are given in Tables V and VI. Again data for pure water and 1 M NaCl reported previously [2] are included for comparison.

The low concentrations of salt, i.e. 0.154 M NaCl and artificial saliva both gave cements that were not significantly different in strength from those made with pure water. In the context of this work, this means that differences were well below the 95% significance level (see Table VII). The higher salt concentrations, though, i.e. 1 M and saturated brine, both gave much weaker cements, with differences being significant at better than the 99% confidence level. The cements made from saturated brine was itself significantly weaker than that made from the 1 M solution. Thus the trend of reduction in strength with increasing salt concentration was shown to continue to an extremely low strength at the most concentrated salt solution possible.

Table VIII shows results for the compressive strength of the zinc polycarboxylates made with various salt solutions. Although there were differences in the mean strengths recorded, they were not statistically significant (see Table VIII). In other words, the presence of salt at any of the levels at which it

TABLE V Compressive strength of glass polyalkenoate

Activating liquid	Compressive srength (Mpa)	Standard deviation (MPa)
Pure water	85.3	9.5
0.154 M NaCl	79.2	9.0
1 M NaCl	53.1	4.7
Saturated NaCl	18.0	3.6
Artificial saliva	87.0	5.8

TABLE VI Compressive strength of zinc polycarboxylate

Activating liquid	Compressive strength (Mpa)	Standard deviation (MPa)
Pure water	95.2	7.1
0.154 M NaCl	90.1	8.8
1 M NaCl	87.2	7.5
Saturated NaCl	could not be mixed	–
Artificial saliva	94.7	8.5

TABLE VII Significance level of differences between compressive strengths of glass polyalkenoates

Activating liquid	Compared with water	Compared with 1 M NaCl
0.154 M NaCl	not significant	99%
1 M NaCl	99%	–
Saturated NaCl	99%	99%
Artificial saliva	not significant	99%

TABLE VIII Significance level of differences between compressive strengths of zinc polycarboxylates

Activating liquid	Compared with water	Compared with 1 M NaCl
0.154 M NaCl	not significant	not significant
1 M NaCl	not significant	–
Artificial saliva	not significant	not significant

remained possible to mix the cement did not affect the final structure of the cement.

This finding confirms conclusions from the earlier work that, in general, the presence of salt does not affect the compressive strength of a zinc polycarboxylate cement. This is assumed to be because the zinc polycarboxylate cement is made of only a matrix of neutralized zinc polyacrylate with unreacted zinc oxide particles embedded in it, and although its speed of formation can be varied, the final structure, and hence its final strength, cannot be altered. By contrast, the complex sequence of reactions, involving hydration of fragments of silica or phosphate assumed to occur as glass polyalkenoate cements set [5, 6], seem markedly affected by the presence of sodium salts in the aqueous phase [2]. The extent to which these reactions can take place to build up a strong matrix seems readily altered, as indicated by the measured differences in compressive strength.

4. Conclusions

The results reported in this paper show that the effect of sodium chloride in polyelectrolyte cements depends on concentration. Effects that had previously been observed with 1 M NaCl were magnified in saturated brine, the highest possible concentration, so that the zinc polycarboxylate set too rapidly to be mixed, and the glass polyalkenoate had a strength of only 18 MPa (compared with 85 MPa when mixed with pure water).

The two solutions containing very low concentrations of NaCl, either alone at 0.154 M, or in artificial saliva, showed no significant effects on the compressive strength of the set cements, but did influence the speed of setting. In both cases, the low concentration solutions increased the speed of the setting reactions, with zinc polycarboxylate being more affected. The possible practical concern that contamination with saliva might lead to weaker cements has been shown to be unfounded, though such contamination would lead to shorter working times and a sharper overall set.

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